Decoding the Fine Flavour Properties of Dark Chocolates

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Cocoa and chocolate key odorants

Aroma development along the processing chain

Harvest → Fermentation → Drying/Transportation → Roasting → Conching → Final Product

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Cocoa and chocolate key odorants

- bell pepper-like
- bergamot-like
- fruity
- banana-like
- dried fruits, flowery
- cinnamon-like
- flowery, rose-like
- honey, beeswax-like
- sweaty, cheesy
- pungent
- seasoning
- phenolic, horse-like
- smoky
- spicy, clove-like
- vanilla-like
- coconut-like
- malty, cocoa-like
- caramel-like
- cooked potato-like
- earthy, roasty
- earthy
- popcorn-like
- cabbage-like
Cocoa and chocolate key odorants

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Cocoa and chocolate key odorants

bell pepper-like  bergamot-like  fruity  banana-like  dried fruits, flowery  
cinnamon-like  flowery, rose-like  honey, beeswax-like  sweaty, cheesy  pungent  seasoning  
phenolic, horse-like  smoky  spicy, clove-like  vanilla-like  coconut-like  
malty, cocoa-like  
caramel-like  cooked potato-like  earthy, roasty  earthy  popcorn-like  cabbage-like
Cocoa and chocolate key odorants

- Bell pepper-like
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- Dried fruits, flowery
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- Sweaty, cheesy
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- Seasoning
- Phenolic, horse-like
- Smoky
- Spicy, clove-like
- Vanilla-like
- Coconut-like
- Malty, cocoa-like
- Caramel-like
- Cooked potato-like
- Earthy, roasty
- Earthy
- Popcorn-like
- Cabbage-like

Compounds present in unfermented fresh cocoa beans:
- Compounds mostly formed during fermentation:
- Compounds mostly formed during thermal processing:

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Chocolate Aroma Analysis

Sample work-up

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Chocolate Aroma Analysis

Identification of odor-active compounds with gas chromatography-olfactometry (GC-O)

Chetschik, I. Key Odorants of Cocoa. *Chimia* 2021, 75, 981.

Aroma Extract Dilution Analysis (AEDA)

Source: Steinhaus, PhD-Thesis 2001
Chocolate Aroma Analysis

Quantification by gas chromatography-mass spectrometry using isotopically substituted odorants

Odor activity value (OAV)/
Dose over threshold factor (DoT factor)

\[ \text{OAV/DoT factor} = \frac{\text{concentration}}{\text{odor threshold}} \]
Chocolate Taste

Alkaloids - bitter
- theobromin
- stimulating compounds
- no significant changes during fermentation & processing
- ratio theobromine/coffeine for differentiation between Forastero/Criollo varieties

Organic acids - sour
- citric acid
- lactic acid
- acetic acid
- citric acid is already present in unfermented cocoa beans
- lactic acid and acetic acids as fermentation products
- acetic acid can be removed by thermal processing

Polyphenols – bitter/adstringent
- epicatechin
- proanthocyanidine
- bitter, rough adstringent
- antioxidative properties → health beneficial effects

Diketopiperazines (DKPs) - bitter
- 27-34
- 35-50
- formed mostly during roasting
- synergistical effect on bitterness with caffeine

Dose over threshold factor (DoT factor)

\[
\text{DoT factor} = \frac{\text{concentration}}{\text{taste threshold}}
\]

Cocoa key tastants according Stark et al, 2005 (figure ZHAW Research Group Food Chemistry)
Perspectives of Cocoa Flavour Research

In the past:
Flavour research mostly done on intermediates/products produced in big industrial scale (no defined origin/variety)

➢ Key compounds of cocoa/chocolate flavour have been identified
➢ Focus: Effect of technological processing on flavour

Today:
➢ More and more consumers demand flavourful, fairly traded, sustainable and traceable products
➢ The scene of small batch producers is growing
   → awareness for a broad range of different cocoa flavours
Flavour diversity of cocoa and chocolate described on sensory level

➢ products of defined variety/origin show different flavour properties than products produced in an industrial scale

➢ Such products have not been studied comprehensively with the methods of the molecular science

➢ The molecular background of fine flavour properties like fruity, cocoa-like and floral is not fully understood yet

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<thead>
<tr>
<th>Origin</th>
<th>Cocoa type</th>
<th>Duration (days)</th>
<th>Special flavor character</th>
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<tbody>
<tr>
<td>Ecuador</td>
<td>Nacional (Arriba)</td>
<td>2 Short</td>
<td>Aromatic, floral, spicy, green</td>
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<td>Ecuador</td>
<td>Criollo (CCN51)</td>
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<td>Acidic, harsh, low cocoa</td>
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<td>Ceylon</td>
<td>Trinitario</td>
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<td>Floral, fruity, acidic</td>
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<td>Venezuela</td>
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<td>Low cocoa, acidic</td>
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<td>Venezuela</td>
<td>Criollo</td>
<td>2</td>
<td>fruity, nutty</td>
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<tr>
<td>Zanzibar</td>
<td>Criollo</td>
<td>6 Medium</td>
<td>Floral, fruity</td>
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<tr>
<td>Venezuela</td>
<td>Forastero</td>
<td>5</td>
<td>Fruity, raisin, caramel</td>
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<td>Ghana</td>
<td>Forastero</td>
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<td>Strong basic cocoa, fruity notes</td>
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<td>Malaysia</td>
<td>Forastero/Trinitario</td>
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<tr>
<td>Trinidad</td>
<td>Trinitario</td>
<td>7–8 Long</td>
<td>Winy, raisin, molasses</td>
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<tr>
<td>Grenada</td>
<td>Trinitario</td>
<td>8–10</td>
<td>Acidic, fruity, molasses</td>
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<tr>
<td>Congo</td>
<td>Criollo/Forastero</td>
<td>7–10</td>
<td>Acidic, strong cocoa</td>
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<tr>
<td>Papua New Guinea</td>
<td>Trinitario</td>
<td>7–8</td>
<td>Fruity, acidic</td>
</tr>
</tbody>
</table>

# Sensory References

**sensory reference samples**

- samples with distinct flavour attributes
- essential for the global standardisation of sensory assessments of cocoa and chocolate
- from *Cocoa of Excellence*
- chocolates produced out of reference liquors (75% cocoa mass, 25% sugar)

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<th>sample code</th>
<th>cocoa variety</th>
<th>cocoa bean origin</th>
<th>reference attributes</th>
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<tbody>
<tr>
<td>Ref1</td>
<td>Forastero</td>
<td>Ghana</td>
<td>cocoa, roast degree</td>
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<td>Ref2</td>
<td>Criollo</td>
<td>Mexico</td>
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<td>Ivory Coast</td>
<td>cocoa, roast degree</td>
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Aim of the Investigation

- Decoding the fine flavour properties of chocolates produced of reference liquors deriving from the *Cocoa of Excellence* Program

- Better understanding the fine flavour attributes for the future development of standardised training samples for sensory panels
Results – GC-O Analysis

GC-O analysis (AEDA)

➢ 47 odor-active compounds were identified
➢ all were known cocoa and chocolate odorants
➢ the distinct fine flavour properties have to be caused by quantitative differences of known key odorants
➢ quantitation of 27 odorants and 8 tastants

Results - GC-O Analysis

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Results - PCA

Principal Component Analysis

Dose over threshold factor (DoT factor) = concentration / odor/taste threshold

Results - Decoding the Fine Flavor Properties of Dark Chocolates

- Ethyl 2-methylbutanoate
- 3-methylbutyl acetate
- Ethyl 3-methylbutanoate
- Ethyl phenylacetate
- Acetic acid

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Results - Decoding the Fine Flavor Properties of Dark Chocolates

4-hydroxy-2,5-dimethylfuran-3(2H)-one

2-methylbutanal

dimethyltrisulfane

3-methylbutanal

phenylacetaldehyde

fruity, acidic
cocoa-like, roast degree
floral, bitter, astringent

Zurich University of Applied Sciences

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Results - Decoding the Fine Flavor Properties of Dark Chocolates

**procyanidin C1**

**(-)-epicatechin**

**procyanidin B2**

**2-phenylethan-1-ol**
Results - Decoding the Fine Flavor Properties of Dark Chocolates – Summary

Ref5: floral, astringent, bitter
Ref1, Ref6: cocoa-like, roasty
Ref2, Ref3, Ref4: fruity, acidic

- **2-phenylethan-1-ol** polyphenols
- 2- & 3-methylbutanal
- 4-hydroxy-2,5-dimethylfuran-3(2H)-one
- dimethyltrisulfane
- ethyl 2-methylbutanoate
- ethyl 3-methylbutanoate
- 3-methylbutyl acetate
- acetic acid
Results - Decoding the Fine Flavor Properties of Dark Chocolates – Outlook

Understanding the fine flavour attributes is important for

- the development of standardised training samples for sensory evaluation of cocoa products and the future quality assessment of cocoa and chocolate
- understand the diversity of chocolate flavours and further research of fine flavour cocoa products e.g. single-variety small batch chocolates
- finding objective indicators for fine or flavour cocoa
- the biodiversity of cocoa, fair cocoa farming and sustainability of cocoa
Thank you for listening!

Decoding the Fine Flavor Properties of Dark Chocolates